5-1-1943

Electrolytic Deposition of Iron

Irving M. Kenoffel

Kenoffel, I. W.

Electrolytic Deposition of Iron

by

Irving M. Kenoffel

A Thesis
Submitted to the Department of Metallurgy
In Partial Fulfillment of
the Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

Montana School of Mines
Butte, Montana

May 1, 1943

Electrolytic Deposition of Iron

by

Irving M. Kenoffel

A Thesis

Submitted to the Department of Metallurgy

In Partial Fulfillment of

the Requirements for the Degree of

Bachelor of Science in Metallurgical Engineering

Montana School of Mines

Butte, Montana

May 1, 1943

Contents

Page 1-- Abstract

Introduction

Page 4-- Further Uses of Electrolytic Iron

Page 7-- Researches on the Electrodeposition of Iron

Page 17-- Tests performed in Laboratory

Page 22-- Test for Carbon

Conclusions

Page 23-- Acknowledgment

Page 24-- Bibliography

Abstract

In this thesis the purpose was to obtain a good iron deposit from a relatively simple bath. The deposit was to be of good nature and low in Carbon content. Also included is a summary of the uses to which electrolytic iron can be put as well as a summary of work done by other researchers in depositing iron electrolytically.

Introduction

Although it has been known since 1860 that iron can be electro-deposited from its solutions, the process has found very little commercial application except in the refining of iron, i.e. the preparation of pure iron for special purposes. It was used for some time in Russia for making or coating printing plates, for which it seems to have had a suitable hardness. In recent years, interest in iron deposition has been renewed because of its successful application during the war for building up worn or undersized parts of military equipment.

In view of the cheapness and availibility of iron, some surprise has been expressed that its deposition has not been more extensively applied for purposes other than refining. The reasons for this apparent neglect of iron deposition are not,

however, difficult to find. Iron plating is not deserving of consideration for either protection or appearance, because of the ready corrodibility of iron, expecially the electrolytic iron. Since a large part of the plating industry involves the coating of iron or steel with other metals for decoration or protection, there is little field for iron plating for such purposes. In the manufacture of printing plates there has been a demand in recent years for a surface more durable than copper. This demand has been met so successfully by the use of nickel that it is now not unusual to secure as many as 2,000,000 impressions from a nickel electro type, a number which is greater than is usually desired except in unusual cases, such as the printing of government securities, carbons, bread wrappers, etc. For such demands or for printing on leather or rough cardboard, etc., it is admitedly desirable to secure harder surfaces, which is now being successfully accomplished by means of chromium. Iron deposition, possible followed by case hardening, may be advantageous for specific purposes. Any such development will usually depend upon a definitely superior service of the iron, and not upon its cheapness. On an ordinary nickel electrotype the

actual cost of the nickel surface (which is usually less than .025 mm. or .001 in. thick) is much less than 1 per cent of the cost of the finished plate, so there would be relatively little economy in the substitution of iron for nickel. For very thick plates however the smaller cost of the iron may represent a real economy.

Even in that field in which the process was recently used successfully, i.e. the building up of parts, there is no evidence that the deposited iron is necessarily harder than nickel, and it is probable that nickel might have been used for this purpose if adequate supplies of it had been available in England and France. In America, Nickel was not infrequently deposited upon undersized shells or other equipment. The greater experience of practical platers with Nickel deposition made its application immediately possible without the necessity of extended research. Now, however, as the result of extensive studies, a large fund of information has been secured, and after greater practical experience it appears probable that iron deposition will be extensively used. Whenever large-scale operation is involved, the lower cost of the iron and iron compounds and the use of high current densities favor the use of iron. In those applications in which case-hardening is practicable, iron deposits have

a unique value. Electrolytic iron tubes have been successfully produced abroad, and in recent years electroforming with iron has also been investigated in this country and in Canada. Thus far however it has not proven practicable in America to produce electrolytic iron tubes at a price to compete with drawn tubes. Further research and development will be required to yield success in this field.

Iron depositing baths possess most of the characteristics and show many of the same defects as nickel baths, and in addition have the disadvantage that there is a tendency for ferrous salts to oxidize to ferric especially when the solutions are nearly neutral. In consequence, the solutions tend to change in composition, and especially in acidity, and require rather frequent regulation. *

Further Uses of Electrolytic Iron

Electrolytic iron when deposited by the usual methods is brittle due to the hydrogen present. In this form it can be easily broken into small pieces and even ground into powder. By heating the iron to a red heat the hydrogen is driven off and the iron becomes ductile, the ductility increasing with the temperature of annealing.

Bib. 1

Brittle electrolytic iron as deposited is highly soluble in acids, being much more readily soluble than Zinc. Annealing the iron makes it become much more resistant to acid attack than ordinary irons and steels. This property of the brittle iron has resulted in the suggestion that it be used for the manufacture of hydrogen by acid attack in place of zinc and other forms of iron.

The brittleness of the iron and its purity make it an ideal material for melting in crucibles, the hydrogen contend having the additional virtue of forming a reducing broken into small pieces for introduction into the crucible.

It may also be used for pharmaceutical purposes as a base for compounds of which iron is a constituent. Here again its purity is of value.

The much suggested use of electrodeposited iron for electro-magnetic purposes appears to be becoming of commercial importance. While the magnetic qualities of electrolytic iron seem to be superior to the commercial silicon irons its high electrical conductivity counteracts this favorable property.

Electrolytic iron also is used as a basis for scientific experimental work on the various pro-

perties of iron where the purest available iron is needed to secure the most accurate data. It is also used as a basis for "pure iron" alloys.

The materials that have been produced and which seem to give the most promise for direct production without further mechanical working are sheets and tubes. By producing directly by deposition in such a manner as to not require further operations it would be possible to make thin sheets and tubes of great uniformity. In tubes having thin walls made by mechanical processes, these often vary in thickness and it is hoped that this defect will be overcome by making them electrolytically.

Also:

Electrolytic iron is likely to come into use as a raw material for making high quality steels by melting in a crucible furnace or electric furnace--the total impurities (excluding hydrogen) are usually only about .03-.04 per cent. The sheets are highly suitable for stamping while the ductility of the metal (after annealing) gives a considerable value to electrolytic iron tubes. Electrolytic iron has a rather high electrical conductivity.

Also:

Electrolytically pure iron can be used for

investigations having for their object the determination of the influence of various elements alloyed with iron as regards its electrical properties etc. Electrolytic iron naturally offers the means of manufactureing chemically pure compounds for standardizing solutions in the analytical chemical laboratory. By reason of the brittleness imparted by the occluded hydrogen it can be readily broken up into grains of a desired size and even reduced to a fine powder. *

Researches on the Electrodeposition of Iron

A careful consideration of the numerous solutions proposed for the deposition of iron makes the following matters clear:

1. The solutions proposed may be divided into three groups, namely, (I) those based upon the use of sulphate of iron; (II) those based upon the chloride, and (III) those containing both sulphate and chloride.

2. A difference of opinion exists as to whether the solution should be neutral or acid.

The Relative Values of the Sulphate and Chloride Baths

The chloride bath centainly has advantages over the sulphate solution in the following respects:

Bib. 2 & 3

(a) It can be made more concentrated on account of the greater solubility of chloride of iron; it can, therefore, contain more metal-iron.

(b) It is a better conductor of the current, generally speaking. Hence, a lower voltage is required, and the bath is, thus, cheaper to work.

(c) In general, the rate at which the chloride bath can be worked, i.e. the current density employable, is greater than in the case of the sulphate solution.

On the other hand, the sulphate bath is preferable to the chloride solution in the following respects:

(a) It can, in many cases, be worked at the ordinary temperature, and can always be worked at a temperature not much above normal, whereas chloride baths almost always require a much higher temperature.

(b) The oxidation of the solution is, in almost all cases, less.

(c) The deposits oxidize very much less quickly than do deposits from the chloride baths. This seems generally recognized by those who have worked with both types of baths.

The Chloride-Sulphate Baths

This third group of solutions for iron deposition includes some baths which appear to have given great satisfaction to their authors, e.g., Varrentrapp's, Watts and Li's, and others. The great objection to "mixed" electrolytes is the difficulty of control, whether scientific or practical, especially on the anode side of the bath. With both chloride and sulphate in the solution it is almost impossible to know what the reactions, chemical and electrochemical, will be at the anode. And, from the practical point of view, though a bath of complex composition may give good results for a time, it will not always do so, and, when something goes wrong, it will be much more difficult to ascertain what the trouble is and, when found, to put things right. Simplicity of composition must, therefore, always be advisable where it can be obtained. Hence, where two solutions, one simple and the other complex give approximately the same good results, the simple one is to be preferred. In the case of iron baths, some of those containing only one anion give quite as good results as any of those containing more than one; there is, consequently, no reason to use one of the latter.

Acid Vs. Neutral Baths

It appears that slight acidity is beneficial, at any rate in the case of the sulphate baths. Slight acidity hinders oxidation of the solution, and prevents the formation of basic salts at the cathode. It, further, improves the conductivity, and enables a considerably higher current density to be employed without injury to, and frequently to the benefit of, the deposit; but slight acidity is all that should be employed. If any considerable quantity of free acid be present, the cathode efficiency suffers in a marked manner; loss of efficiency is scarcely noticeable with slight acidity. Moreover, the presence of considerable free acid causes a distinct diminution in the size of the grains of which the deposit consists, accompanied by a distinctly increased hardness and brittleness.

The Purpose of the Deposition

The purpose for which the deposit is required is, usually, not sufficiently borne in mind, when this or that solution is adopted for obtaining an iron deposit. Yet it is essential that the solution should suit the desired object. For instance, it is no purpose that a bath containing organic salts or other like substances is selected for the deposition of pure iron. Again, a solution used for

steel-facing must be one that will give a thin layer of very hard iron. Color is unimportant in this case, as also is thickness. A deposit that would be of sufficient thickness for steel-facing will often crack up and peel off the base metal, if deposition be continued. The truth is that, as in the case of solutions used for the electrodeposition of other metals, nickel, zinc, tin and others, no one iron solution is of what may be called the "universal" type, or one suited to every purpose.

Group 1

Sulphate Solutions

(1) C. Hoepfner and Klie's Solution

These investigators do not appear to have published anything respecting their work on iron deposition; information regarding it has to be obtained from other sources.

K. Arndt states of the work of Hoepfner and Klie, "Dr. Klie has in 1895 deposited iron under the following conditions: Bath-A weakly acid solution of 462 grams $FeSO_4$ plus 75 grams $(NH_4)_2SO_4$ in 1.5 liters water. Cathode-Copper sheet, rubbed with vaseline and sprinkled over with powdered graphite. Anode-Cast iron plate. Diaphragm-Thin porous plate inserted in a frame between the anode

and cathode. The bath temperature was maintained at 70° to 80°C., the current density was about 3 amp./sq. dm., and the voltage amounted to .75 volt.

Arndt mentions that the process was not followed up, as no economic use for chemically pure electrolytic iron was present to Hoepfner's mind.

(2) Klein's Solution

The solution which is usually referred to as "Klein's" is one that is based upon ferrous sulphate, as the metal salt, and contains magnesium sulphate, as the conducting salt. There are not any details of the bath published in the literature of Klein himself; but information respecting it has been given by others.

(a) F. Haber on Klein's Solution. This authority states that he obtained faultless deposits from Klein's bath under the following conditions: Composition-.5g. mol. of $MgSO_4$ aq. and the same weight of $FeSO_4$ aq. to each liter of water. Current density-.25 amp./sq.dm. Cathode--Lacquered sheet (copper). He found that when he deposited the iron tube(which served as anode), the deposit showed a tendency to split up; but that if the cathode cylinder was rotated, deposits up to .15 mm. thick could be obtained (and at the relatively high

current density of from .4 to .42 amp./sq.dm.) without any sign of peeling.

(b) S. Maximowitsch on Klein's Solution-Modified. An accumulator cell, of six liters content, was filled with a solution of 20 percent. $FeSO_4$ aq. and 5 percent $MgSO_4$ sq., and two iron electrodes were suspended in it. The cathode was a copper plate, lightly "silvered and iodized." Twenty-five grams of $NaHCO_3$ were added to the solution. This caused a dirty yellow foam to form on the surface which c changed after three days into a brown skin. The solution gradually cleared, with the separation of a voluminous precipitate. Twice a week, from 20 to 25 grams of the bicarbonate were added, and this was continued for four weeks, by which time some 186 grams of bicarbonate had been added, which was sufficient to precipitate the iron from 300 grams $FeSO_4$aq., that is from 25 percent of the total amount of iron salt used. Under the skin of ferric hydrate the solution was protected from atmospheric oxidation, and became quite clear. The content of $Fe(CO_3H)_2$ was found to be .23 percent.

The iron obtained proved quite exceptionally suited to the preparation of printing plates. It attained a tensile strength of 5,180 kg./sq. cm.,

yet, was so flexible that it could be sharply bent without breaking. The best current density was .3 amp./sq. dm.

(3) C.F. Burgess and C. Hambuechen's Solution

The electrolyte consists of ferrous and ammonium sulphates; the current density at the cathode is 6 to 10 amp./sq. ft. and at the anode slightly less; the electromotive force for each cell is slightly under one volt; the temperature of the electrolyte is about 30° C.; the anodes consist of ordinary grades of wrought iron and steel; the starting sheets for the cathodes are of thin sheet iron, previously cleaned of rust and scale.

Analyses of the deposited iron exceed 99.9 percent purity. The only impurity which has been detected is hydrogen. The hydrogen can be driven off almost completely by heating to a white heat, the evolution commencing at a temperature below a red heat. The metal is hard and brittle, as taken from the tanks; but, after being heated at a welding temperature, assumes properties of malleability and toughness similar to those of Swedish iron.

(4) R. Amberg's Method

Amberg aimed at producing 1 kg. of pure iron per week. To that end he worked on a 30 liter scale. $FeSO_4$ and an equivalent amount of $(NH_4)_2SO_4$ was

dissolved in water in such quantity that the solution contained 15 to 45 grams of iron per liter. The surface of the solution was covered with a layer of solid paraffin. Two bars of Krupp's iron, wrapped in linen bags, were placed in the center of the trough, and on each side was suspended a cathode sheet of iron or copper. The solution was sometimes agitated with a glass stirrer. The iron content of the deposit, after driving off the hydrogen, was over 99.9 percent.

(5) A. Pfaff's Solution

This author says: " As the result of my researches, I find the following to be the most suitable conditions for the electrolytic separation of iron in thick layers:

2N ferrous sulphate solution

.01 N sulphuric acid

Current density (cathode) 18.5 amp./sq.ft.

Temperature, 70°C

Pfaff removes the hydrogen bubbles, adhering to the work, by blowing air into the solution ; this also agitates the solution. It is to be noted that he uses a slightly acidified bath, and makes a point of the importance of this. An objection to Pfaff's system might be in blowing air into the solution as a solution of ferrous sulphate is readily oxidized.

(6) W.A. Macfadyen's Investigations

Macfadyen investigated the possibilities of the sulphate solution, both cold and hot, neutral and acid; but he does not appear to have discovered anything essentially new. Summarizing his results, he states: "An aqueous solution of ferrous ammonium sulphate was the electrolyte used, and it was found that whilst excellent results could be obtained from dilute solutions at the room temperature, deposition could only be carried out very slowly; with a concentrated solution, however, equally good results were obtained at about seven times the rate usuable in the former case.

(7) M. Schlotter's Process

A solution containing 150 grams of ferrous sulphate and 100 g. of sodium sulphate per liter is treated with sufficient sodium carbonate to neutralize any free acid. The solution is worked at or near boiling point, and a current density of 20 amp./sq. ft. is employed.

It is claimed that the deposit contains very little hydrogen and is of great purity, and it is pointed out that lead-lined vats and heating pipes can be used.*

Group II

Bib. 4

Chloride Solutions

Since no work was done on Chloride solutions, and all investigations were made on sulphate solutions, we shall omit discussion of the various types of baths that fall into this category.

The purpose of my deposition was to obtain iron pure with respect to Carbon, and also to obtain a bright deposit. The bath used was strictly a sulphate bath and contained only $FeSO_4\ 7H_2O$ and $(NH_4)_2\ SO_4$. The idea was to pick amounts of these two salts which would form an electrolyte that would give a fairly good deposit. The procedure from there was to try various addition agents to see if the nature of the deposit could be improved, and after this to again vary the composition of the two sulphate salts to further improve the deposit.

Test No. 1

Electrolyte:

150 g. $FeSO_4\ 7H_2O$

120 g. $(NH_4)_2SO_4$ per liter

Current Density:

19 amps./sq. ft.

Anode:

Low Carbon Steel--.15% C

Cathode:

Copper sheet

Nature of Deposit:

Fair, not bright, brittle and slightly pitted

Test No. 2

Electrolyte:

Same as in 1

Current Density:

Same as in 1

Anode and Cathode are the same

Addition Agent:

20 grams Aluminum sulphate/liter

Nature of Deposit:

Rough, pitted, black brittle, worthless

Test No. 3

Same set up as in 1

Addition agent:

20 cc. Diethyl Carbonal/liter

Nature of Deposit:

Fair, rusted, no good after exposed to air

Test No. 4

Same set up as in 1

Addition agent:

10 g. Boric Acid/liter

Nature of Deposit:

Bright but not smooth, brittle and crumbly

Test No. 5

Same set up as in 1

Addition agent:

10 g. Oxalic acid/liter

Nature of Deposit:

Smooth bright and brittle

Test No. 6

Same set up as in 1

Addition agent:

4 drops formaldehyde

Nature of Deposit:

Good, smooth and bright

Test No. 7

Same set up as in 1

Addition agent:

.5 g. licorice/liter

Nature of Deposit:

Poor, much pitted

Test No.8

Same set up as in 1

Addition agent:

2 drops turpentine

Nature of Deposit

Poor, light gray and badly pitted

Test No. 9

Same set up as in 1

Addition agent:

10 g. ammonium oxalate

Nature of Deposit:

Smooth, bright, no holes or pits

At this point it can be noted that the best deposit was obtained when the oxalate radical was present as an addition agent, and that the deposit obtained when Ammonium oxalate was used was better than that obtained when Oxalic acid was used.
The next part of the experiments consisted in varying the concentration of the two sulphate salts and leaving the ammonium oxalate as the addition agent.

Test No. 10

Electrolyte:

$FeSO_4$ $7H_2O$ - 250 g. per liter

$(NH_4)_2\ SO_4$ - 120 g. per liter

Everything else was left constant

Nature of Deposit:

Rough, pitted, rusty yellow in color

Test No. 11

Electrolyte:

$FeSO_4\ 7H_2O$ --150 g.
$(NH_4)_2SO_4$ -- 75 g. } per liter

Everything else was left constant

Nature of Deposit:

Smooth, close grained, greenish in color, not bright.

Test No. 12

Electrolyte:

$FeSO_4\ 7H_2O$ --150 g.
$(NH_4)_2SO_4$ -- 100 g. } per liter

Everything else was left constant

Nature of Deposit:

Excellent, smooth, silvery white--best yet.

At this point no further tests were made as the bath indicated in test 12 fulfilled all the requirements. Deposition was continued using this bath until a considerable amount of iron was

obtained and then a Carbon content test was performed on it.

Test for Carbon

This test was performed using a CO_2-O_2 train.

Wt. of iron sample--2.7273 g.

Wt. of vessel & CO_2-- 138.5698

Wt. of vessel & O_2 -- 138.5686

.0012-- .012 %C

The iron contained .012% C which is considered very pure for most purposes. Original C content was .15%C.

All electrolytic tests were performed using a 400 cc. beaker as the cell and at a voltage of 2 volts. The time of electrolysis was 24 hours in all tests. It can be noted here that the deposits obtained using test 12 began to get rough and pitted after 48 hours, which appears to be the time limit for this bath. The deposit at the end of this maximum time, however, was quite thick.

Conclusions

The tests show that a very desirable deposit can be obtained by the use of a simple sulphate bath plus one addition agent. This is of importance in considering expense etc. If more time was

available I would have liked to perform similar tests using a Chloride bath. This would be a good topic for a thesis for someone at some future time.

Acknowledgment:

I wish to acknowledge the help and supervision of Dr. C. Fulton and Professor M.C. Smith in preparing this thesis. Their cooperation in giving advice and obtaining equipment is greatly appreciated.

Bibliography

1. Principles of Electroplating and Electroforming
   by Blum and Hogaboom
   "Iron Deposition"
2. T.A.E.C.S. Vol. 29
   by Oliver W. Storey
   Uses of Electrolytic Iron
3. Metals and Metallic Compounds -Vol 3
   by Evans
   Uses of Electrolytic Iron
4. T.A.E.C.S. Vol. 40
   by W.E. Hughes
   Researches on the Electrodeposition of iron
5. T.A.E.C.S. 1904
   C.F. Burgess and C Hambuecher
   "Electrolytic Iron"
6. Iron Steel Inst. 9D
   by L. Guillet
7. Chem. Met. Eng. Vol. 26
   by W.E. Hughes